

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : KANSAI PAINT CO LTD

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(72)Inventor : TAKAMI SEIJI

HIDAKA TAKAHIRO

## (54) ULTRAVIOLET-CURABLE COATING COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a coating composition capable of forming a coating film which excels in the adhesion to a printing ink layer and a clear coating film, the external appearance of a coating film, processability, hardness, retorting resistance and the like.

SOLUTION: The ultraviolet-curable can coating composition comprises 100 pts.wt. sum of (A) an oxetane compound having a long chain alkyl group or an alkenyl group, (B) a cationically polymerizable compound other than the above compound (A). (C) 0.01-20 pts.wt. cation polymerization initiator which generates a cation by ultraviolet irradiation, and (D) 1-30 pts.wt. aluminum powder having been treated with stearic acid. A method for producing a coated metallic can comprises coating a metallic sheet, a resin film-laminated metallic sheet or a metallic can with this coating composition, irradiating the coated composition with ultraviolet rays to cure it, subsequently providing printing, and then coating the printed surface with a clear coating to cure it.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ultraviolet curing mold coat formation constituent which can form the metallic paint film with high brightness which was excellent in the adhesion between layers and was excellent also in coat engine performance, such as workability, a degree of hardness, and abrasion-proof nature.

[0002]

[Description of the Prior Art] Conventionally, the cationic polymerization mold coating containing the cationic initiator which generates a cation as an ultraviolet curing mold coating by the cationic polymerization nature compound and UV irradiation which have an epoxy group and a vinyl group, the radical polymerization mold coating containing the radical polymerization initiator which generates a radical by the radical polymerization nature compound and UV irradiation which have a radical polymerization nature partial saturation radical, etc. are known.

[0003] In these ultraviolet curing mold coatings, blending photoluminescent pigment etc. from points, such as improvement in the fine sight of the paint film obtained, is performed, and these people proposed the ultraviolet curing mold coating containing an aluminium powder in JP,2000-273399,A. Although the coating of this proposal could form the outstanding photoluminescent paint film, when a paint film with high brightness was formed as an aluminium powder using the aluminium powder by which stearic acid processing was carried out, and the so-called leafing aluminum and printing ink and a clear coating were applied on this photoluminescent paint film, it had the problem that the adhesion between layers of a photoluminescent paint film, and a printing ink or a clear paint film was not enough.

[0004] Moreover, while there was the description that a cure rate is quick, the above mentioned radical polymerization mold coating had the adhesion to a material, and inadequate workability, and since there was hardening inhibition by oxygen, was inferior to surface hardenability and had the trouble that nitrogen enclosure etc. needed to be furnished, especially on the occasion of use with a thin film (2-8 micrometers).

[0005] The purpose of this invention is offering the ultraviolet curing mold coating constituent which can form the photoluminescent paint film which could harden by UV irradiation, was excellent in the adhesion over a printing ink layer or a clear paint film with the thin film, and was excellent in paint film engine performance, such as a paint film appearance needed as a tin paint, workability, a degree of hardness, and retort-proof nature, without needing the facility containing nitrogen etc.

[0006] Moreover, the purpose of this invention is offering the manufacture approach of a paint metal can of having the luminosity coat which was excellent in adhesion with a printing layer and a clear coat, and was excellent also in brightness, a paint film appearance, and the paint film engine performance.

[0007]

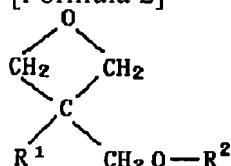
[Means for Solving the Problem] Then, this invention persons observe the cationic polymerization mold coating which can be hardened by ultraviolet rays without needing the facility containing nitrogen etc.

The result of having inquired wholeheartedly in order to obtain the ultraviolet curing mold coating constituent containing the aluminium powder which can form the photoluminescent paint film excellent in adhesion with a printing layer and a clear coat, and can attain the above-mentioned purpose and by which stearic acid processing was carried out, When carrying out constant-rate use of the compound which has the specific oxetane ring which has a long-chain alkyl group or a long-chain alkenyl radical of the compounds of a cationic polymerization nature compound, it came to complete header this invention for the ability of the above-mentioned purpose to be attained.

[0008] In this way, this invention is the (A) following type [1].

[0009]

[Formula 2]



[1].

[0010] R<sup>1</sup> expresses the shape of the shape of a hydrogen atom, a fluorine atom, and a straight chain of the carbon atomic numbers 1-6, a branched-chain or annular alkyl group, and a straight chain of the carbon atomic numbers 1-6, a branched-chain or annular fluoro alkyl group, an allyl group, an aryl group, an aralkyl radical, a furil radical, or a thienyl group among [type, and R<sup>2</sup> expresses the shape of a straight chain, the branched-chain alkyl group, or alkenyl radical of the carbon atomic numbers 6-20. ]

The ultraviolet curing mold tin paint constituent characterized by to contain the cationic initiator 0.01 which comes out and generates a cation by (C) UV irradiation to the total quantity 100 weight section of the oxetane compound 1 shown - 80 weight sections, and cationic polymerization nature compounds 20 other than the (B) above-mentioned compound (A) - 99 weight sections - 20 weight sections, and the aluminium powder 1 with a mean particle diameter of 1-50 micrometers by which (D) stearic acid processing was carried out - 30 weight sections is offered.

[0011] This invention paints the above-mentioned ultraviolet curing mold tin paint constituent again to the metal can which cast a metal plate, resin film laminated metal plates, or these metal plates, and after it irradiates ultraviolet rays and stiffens them, it prints on this hardening paint film, and it offers the manufacture approach of the paint metal can characterized by subsequently painting and stiffening a clear coating.

[0012]

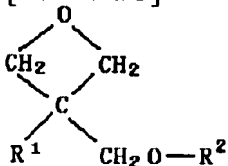
[Embodiment of the Invention] First, the ultraviolet curing mold tin paint constituent of this invention is explained.

[0013] The coating constituent of this invention contains an oxetane compound (A), a cationic polymerization nature compound (B), a following cationic initiator (C), and a following aluminium powder (D) as an indispensable component.

[0014] The oxetane compound which is the (A) component of the oxetane (compound A) this invention coating constituent is the following formula [1].

[0015]

[Formula 3]



[1]

[0016] R<sup>1</sup> expresses the shape of the shape of a hydrogen atom, a fluorine atom, and a straight chain of the carbon atomic numbers 1-6, a branched-chain or annular alkyl group, and a straight chain of the carbon atomic numbers 1-6, a branched-chain or annular fluoro alkyl group, an allyl group, an aryl group, an aralkyl radical, a furil radical, or a thienyl group among [type, and R<sup>2</sup> expresses the shape of a

straight chain, the branched-chain alkyl group, or alkenyl radical of the carbon atomic numbers 6-20. ] It is the compound which comes out, is shown, and can cause and harden cationic polymerization.

[0017] In the above-mentioned formula [1] R1 The shape of a hydrogen atom, a fluorine atom, and a straight chain of the carbon atomic numbers 1-6, a branched-chain or annular alkyl group (for example, methyl, ethyl, n-, or i-propyl --) n-, i- or t-butyl, pentyl, hexyl, a cyclohexyl radical, etc., The shape of a straight chain, branched-chain fluoro alkyl group of the carbon atomic numbers 1-6 for example, monofluoro methyl, difluoromethyl, and trifluoromethyl -- 2, 2, and 2-trifluoroethyl, perfluoro ethyl, perfluoro propyl, Allyl groups, such as perfluoro butyl and a perfluoro hexyl group, an aryl group Or an aralkyl radical (For example, phenyl, naphthyl, tolyl, a xylyl group, etc.) for example, (benzyl, a phenethyl radical), etc. -- expressing --;R2 -- the carbon atomic numbers 6-20 -- desirable -- the shape of a straight chain of 8-18, and a branched-chain alkyl group (hexyl --) Octyl, 2-ethylhexyl, DESHIRU, dodecyl, hexadecyl, the carbon atomic numbers 6-20, such as an octadecyl radical, -- the shape of a straight chain and branched-chain alkenyl radicals of 8-18 (for example, octadecenyl, 3, 7-dodecadienyl, 9, 12-octadecadienyl radical, etc.) are expressed preferably.

[0018] As R1, an ethyl group is suitable especially.

[0019] In the above-mentioned formula [1], when R2 was the shape of a straight chain, the branched-chain alkyl group, or alkenyl radical of the carbon atomic numbers 6-20, this invention constituent should be excelled in adhesion with a printing layer and a clear coat.

[0020] The cationic polymerization nature compounds which are the (B) components of the cationic polymerization nature (compound B) this invention coating constituent are components other than the above-mentioned oxetane compound (A) which can cause and harden cationic polymerization by the above-mentioned UV irradiation.

[0021] The above-mentioned cationic polymerization nature compound can mention one sort of the cationic polymerization nature compound which can be a compound which has a cationic polymerization nature machine, for example, is shown by following (a) - (e), or two sorts or more.

(a) The thing of 80-3,000 can be used suitably preferably. compound: which has an epoxy group -- the compound which has one or more epoxy groups in 1 molecule -- it is -- weight per epoxy equivalent 70-5,000 -- as an example of representation For example, dicyclopentadiene dioxide, methyl (3, 4-epoxycyclohexyl) -3, 4-epoxy cyclohexane carboxylate, The bis(2, 3-epoxy cyclopentyl) ether, a bis(3, 4-epoxycyclohexylmethyl) horse mackerel peat, A bis(3, 4-epoxy-6-methylcyclohexyl methyl) horse mackerel peat, Methyl -3, 4-epoxy-6-methylcyclohexane carboxylate, (3, 4-epoxy-6-methylcyclohexyl) A bis(3, 4-epoxycyclohexylmethyl) acetal, the bis(3, 4-epoxycyclohexyl) ether of ethylene glycol, 3 of ethylene glycol, 4-epoxy cyclohexane-carboxylic-acid diester, Methyl alcohol, ethyltrimethoxysilane (3, 4-epoxycyclohexyl), (3, 4-epoxycyclohexyl) 3-ethyl-3-(3, 4-epoxycyclohexylmethyl) oxymethyloxetane, The epoxy compound containing alicyclic epoxy groups, such as EPOLEAD GT 300 (the Daicel Chemical Industries, Ltd. make, a trade name, 3 organic-functions cycloaliphatic epoxy resin); for example Ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, Polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, neopentyl glycol diglycidyl ether, 1, 6-hexanediol diglycidyl ether, glycerol diglycidyl ether, Diglycerol tetraglycidyl ether, trimethylolpropane triglycidyl ether, Spiroglycol diglycidyl ether, 2, 6-diglycidyl phenyl ether, Sorbitol polyglycidyl ether, triglycidyl isocyanurate, Bisphenol A diglycidyl ether, butadiene dioxide, Phthalic-acid diglycidyl ester, 3-ethyl-3-glycidyl oxymethyloxetane, A halogenation bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, The epoxy compound containing aliphatic series epoxy groups, such as o-, m-, a p-cresol novolak mold epoxy resin, and a phenol novolak mold epoxy resin; for example The epoxy compound containing an alicyclic epoxy group and aliphatic series epoxy groups, such as vinylcyclohexene dioxide and limonene dioxide; the fatty acid which has the carbon atomic numbers 6-33 to the compound which has two or more epoxy groups in 1 molecule among the above-mentioned epoxy compounds (for example) The fatty-acid denaturation epoxy compound which has an epoxy group and a fatty-acid-ester radical in 1 molecule which makes a lauric acid, oleic acid, a linseed-oil fatty acid, etc. come to react to a part of epoxy group, Epoxidation polybutadiene, the glycidyl group content copolymer of a glycidyl group content polymerization nature

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partial saturation monomer and other polymerization nature partial saturation monomers, etc. can be mentioned. These compounds are independent or can be used combining two or more sorts.

[0022] As a glycidyl group content polymerization nature partial saturation monomer which constitutes the above-mentioned glycidyl group content copolymer, glycidyl acrylate, glycidyl methacrylate, etc. are mentioned and an acrylic ester monomer, a methacrylic ester monomer, styrene, etc. can be mentioned as other polymerization nature partial saturation monomers. The above-mentioned glycidyl group content copolymer has at least one glycidyl group in a molecule, and it is suitable for it that glass transition temperature is 30 degrees C.

[0023] As some cationic polymerization nature compounds (B), the adhesion of a paint film, and the ink layer and clear paint film which are obtained from this invention constituent the inside of a total of 100 weight sections of the (A) component and the (B) component, below 40 weight sections extent, and by carrying out 5-30 weight section extent use preferably in the above-mentioned fatty-acid denaturation epoxy compound, epoxidation polybutadiene, or a glycidyl group content copolymer can be raised.

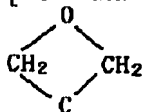
[0024] Vinyl compound : (b) Styrene, alpha methyl styrene, p-chloromethyl styrene, Aromatic series vinyl compounds, such as vinyltoluene; n-butyl vinyl ether, Permutations or unsubstituted alkyl vinyl ether, such as isobutyl vinyl ether, cyclohexyl vinyl ether, and hydroxybutylvinyl ether; Allyl vinyl ether, Alkenyl vinyl ether, such as ethenyl vinyl ether and 1-methyl-2-propenyl vinyl ether; Phenyl vinyl ether, Aryl vinyl ether, such as p-methoxyphenyl vinyl ether; The butanediol divinyl ether, The alkyl divinyl ether, such as triethylene glycol divinyl ether and the cyclohexane diol divinyl ether; 1, 4-benzenedimethanol divinylether, The aralkyl divinyl ether, such as the N-m-chlorophenyl diethanolamine divinyl ether and the m-phenylene bis(ethylene glycol) divinyl ether; The hydroquinone divinyl ether, The aryl divinyl ether, such as the resorcinol divinyl ether; cationic polymerization nature nitrogen content compounds, such as N-vinylcarbazole and N-vinyl pyrrolidone.

[0025] (c) Bicyclo orthochromatic ester compound : 1-phenyl-4-ethyl - 2, 6, a 7-trioxabicyclo-[2, 2, 2]-octane, 1-ethyl-4-hydroxymethyl - 2, 6, 7-trioxabicyclo-[2, 2, 2]-octane, etc.

SUPIRO orthochromatic carbonate compound : (d) 1, 5, 7, a 11-tetraoxaspiro-[5, 5]-undecane, 3, 9-dibenzyl - 1, 5, 7, a 11-tetraoxaspiro-[5, 5]-undecane, 1, 4, a 6-trioxa SUPIRO-[4, 4]-nonane, 2-methyl - 1, 4, a 6-trioxa SUPIRO-[4, 4]-nonane, 1 and 4, 6-trioxa SUPIRO-[4, 5]-Deccan, etc.

[0026] (e) Oxetane ring content compounds other than the above-mentioned oxetane compound (A) : the following type [0027]

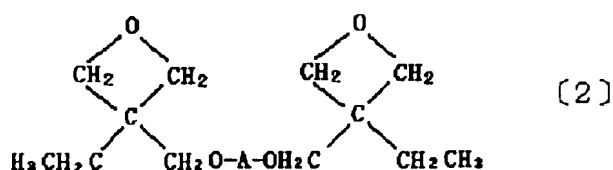
[Formula 4]



[0028] It is the compound which comes out and contains the oxetane ring expressed in [ at least one ] a molecule. As an example For example, 3-ethyl-3-methoxymethyl oxetane, 3-ethyl-3-ethoxymethyl oxetane, 3-ethyl-3-butoxy methyl oxetane, 3-ethyl-3-aryloxymethyl oxetane, 3-methyl-3-hydroxymethyloxetane, 3-ethyl-3-hydroxymethyloxetane, 3-ethyl-3-(2'-hydroxyethyl) oxymethyloxetane, 3-ethyl-3-(2'-hydroxy-3'-phenoxy propyl) oxymethyloxetane, 3-ethyl-3-(2'-hydroxy-3'-butoxy propyl) oxymethyloxetane, 3-ethyl-3-[2'-(2"-ethoxyethyl) oxymethyl] oxetane, 3-ethyl-3-(2'-butoxy ethyl) oxymethyloxetane, 3-ethyl-3-benzyloxymethyl oxetane, 3-ethyl-3-(p-tert-butylbenzyl oxymethyl) oxetane, 3-ethyl-3-glycidyl oxymethyloxetane, 3-ethyl-3-(3, 4-epoxycyclohexylmethyl) oxymethyloxetane, compound [which has bis(3-ethyl OKISETANIRU-3-methyl) oxide, a polymerization nature partial saturation radical, and an oxetane ring -- for example The copolymer which has the oxetane ring which comes to carry out radical copolymerization of the 3-ethyl-3-(acryloyloxyethyl) oxymethyloxetane to 1 monomer component; the following type [2]

[0029]

[Formula 5]

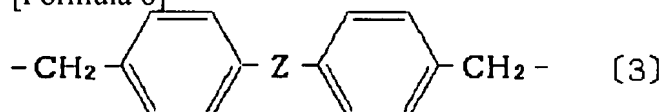


[0030] The compound shown by (A expresses among a formula the divalent hydrocarbon group of the carbon atomic numbers 1-23 which may contain heteroatoms, such as an oxygen atom) can be mentioned.

[0031] the compound expressed with the above-mentioned formula [2] -- setting -- as A in a formula -- the shape of a straight chain, a branched-chain or annular alkylene group (especially alkylene group of the carbon atomic numbers 1-15, such as methylene, ethylene, a propylene, a butylene, and a cyclohexylene radical), and the carbon atomic numbers 4-30 -- desirable -- the polyalkylene oxy-radicals (for example, Pori (ethyleneoxy), the Pori (propyleneoxy) radical, etc.) of 4-8, a phenylene group, a xylylene radical, and the following type [3]

[0032]

[Formula 6]



[0033] The divalent aromatic hydrocarbon radical shown by (Z expresses O, S, CH<sub>2</sub>, NH, SO, SO<sub>2</sub>, C(CF<sub>3</sub>)<sub>2</sub>, or C(CH<sub>3</sub>)<sub>2</sub> among the above-mentioned formula) can be mentioned.

[0034] The above (a) The compound (a) and/or oxetane ring content compound (e) which have an epoxy group (especially alicyclic epoxy group) especially among the compounds of - (e) can be used suitably.

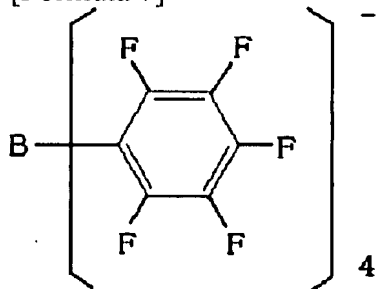
[0035] Into a cationic initiator (C) this invention constituent, in order to promote hardening of this invention constituent by UV irradiation, a cationic initiator (C) is blended.

[0036] A cationic initiator (C) can generate a cation, can make a polymerization able to start by UV irradiation, and can mention the compound expressed with the following type, for example as an optical cationic initiator.

[0037] Ar<sub>2</sub>I<sup>+</sup> and X<sup>-</sup> (I)

Ar expresses an aryl group, for example, a phenyl group, among [type, and X<sup>-</sup> is PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, or the following formula [0038].

[Formula 7]



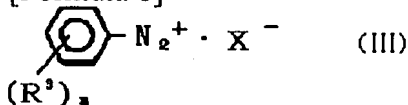
[0039] ] which comes out and shows the radical expressed

Ar<sub>3</sub>S<sup>+</sup> -X<sup>-</sup> (II)

[Ar and X<sup>-</sup> has the same semantics as the above among a formula.]

[0040]

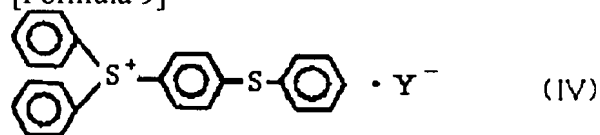
[Formula 8]



[0041] [R3 expresses the alkyl group of carbon numbers 1-12, or the alkoxy group of carbon numbers 1-12 among a formula, n expresses the integer of 0-3, and X- has the same semantics as the above.]

[0042]

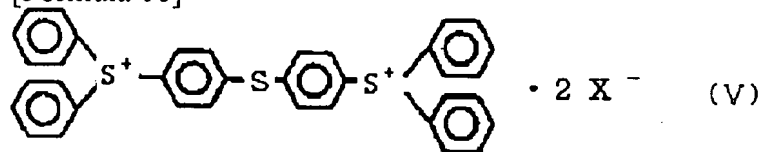
[Formula 9]



[0043] [Y- expresses PF6-, SbF6-, AsF6-, or SbF5(OH)- among a formula.]

[0044]

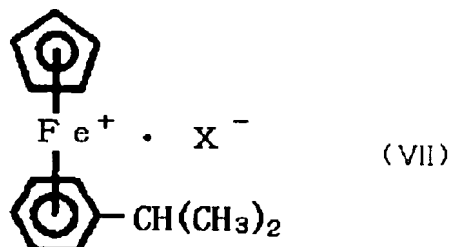
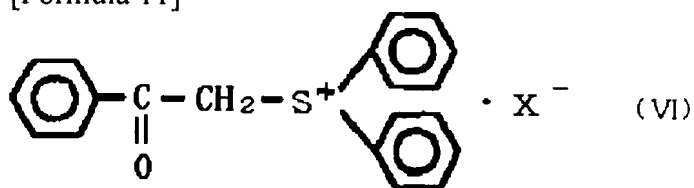
[Formula 10]



[0045] [X- has the same semantics as the above among a formula.]

[0046]

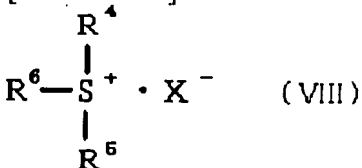
[Formula 11]



[0047] [Each X- has the same semantics as the above among the two above-mentioned formulas.]

[0048]

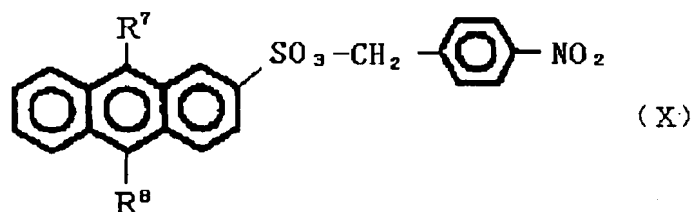
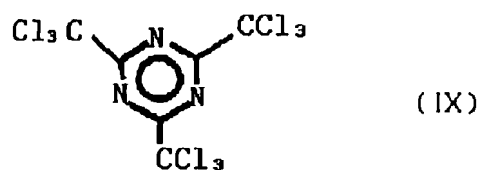
[Formula 12]



[0049] [R4 shows among a formula the alkyl group of the carbon atomic numbers 1-5 in which the aralkyl radical of the carbon atomic numbers 7-15 or the alkenyl radical of the carbon atomic numbers 3-9, and R5 contain the hydrocarbon group or hydroxyphenyl radical of the carbon atomic numbers 1-7, and R6 may contain the oxygen atom or the sulfur atom, and X- has the same semantics as the above.]

[0050]

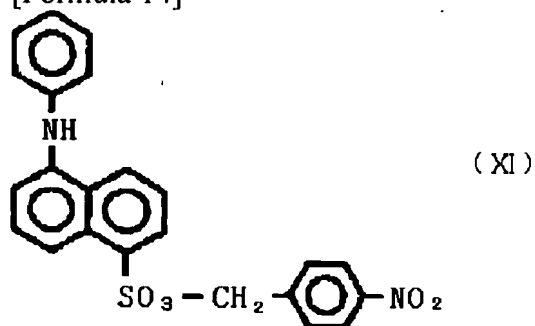
[Formula 13]



[0051] [R7 and R8 express the alkyl group of the carbon atomic numbers 1-12, or the alkoxyl group of the carbon atomic numbers 1-12 independently among a formula, respectively.]

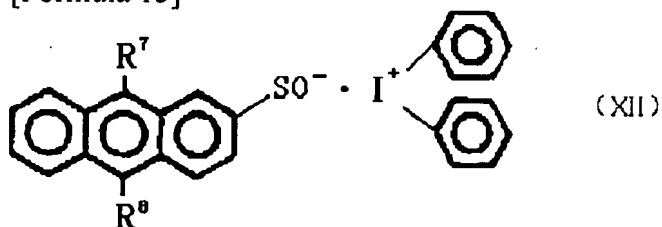
[0052]

[Formula 14]



[0053]

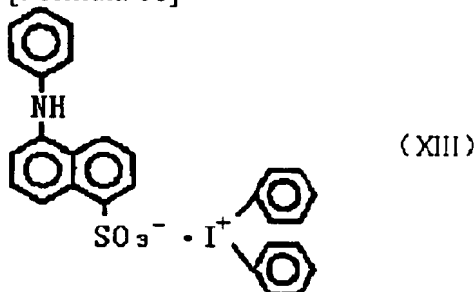
[Formula 15]



[0054] [R7 and R8 have the same semantics as the above among a formula.]

[0055]

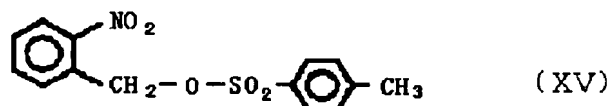
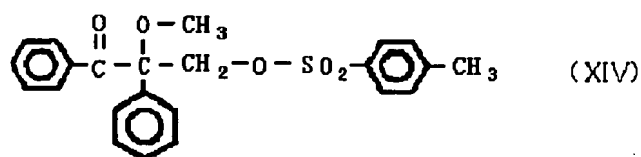
[Formula 16]



[0056]

[Formula 17]





[0057] as the commercial item of an optical cationic initiator -- SAIRA cure UVI-6970 -- said -- UVI-6974 -- said -- UVI-6990 (all are made in [ union carbide company ] the U.S. above), IRGACURE 261 (product made from tiba special tee KEMIKARUZU), CIT-1682 (Nippon Soda Co., Ltd. make), PHOTOINITIATOR (photograph initiator)2074 (Rhône-Poulenc S.A. make), etc. can be mentioned.

[0058] 1-50 micrometers (D50) of mean particle diameter with which the aluminum front face was processed with stearic acid of the aluminium powder (D) which can be used in aluminium-powder (D) this invention are a 3-30-micrometer aluminium powder preferably. When an aluminium powder (D) carries out paint film formation, it can present a metallic appearance with high brightness, and it includes the so-called leafing aluminium powder.

[0059] The blending ratio of coal of the above-mentioned oxetane compound (A), a cationic polymerization nature compound (B), a cationic initiator (C), and an aluminium powder (D) of the ultraviolet curing mold tin paint constituent of this invention is as follows based on a total of 100 weight sections of an oxetane compound (A) and a cationic polymerization nature compound (B).

Oxetane (Compound A):1 - 80 weight section -- desirable -- 5 - 70 weight section and cationic polymerization nature (compound B):20 - 99 weight section -- desirable -- 30 - 95 weight section and cationic initiator (C):0.01 - 20 weight section -- desirable -- 0.5 - 10 weight section and aluminium-powder (D):1 - 30 weight section -- desirable -- 3 - 20 weight section.

[0060] It is suitable from viewpoints, such as the hardenability of a paint film, adhesion, and paint film physical properties, that the blending ratio of coal of the oxetane compound (A) and cationic polymerization nature compound (B) in the coating constituent of this invention is in above-mentioned within the limits. Moreover, it is suitable from the field of \*\*, such as the hardenability of a paint film, and paint film physical properties, that the blending ratio of coal of a cationic initiator (C) is in above-mentioned within the limits. Furthermore, it is suitable from viewpoints, such as brightness of a paint film, an appearance, and paint workability, that the blending ratio of coal of an aluminium powder (D) is in above-mentioned within the limits.

[0061] this invention coating constituent may contain reforming resin, such as polyol resin, phenol resin, acrylic resin, polyester resin, polyolefin resin, and a polybutadiene resin, an organic resin particle, perfume, a solvent, etc. if needed in addition to the above (A), (B), (C), and the (D) component.

[0062] The coating constituent of this invention can mix each component described above, and can prepare it by mixing and agitating so that it may become a uniform coating constituent. For example, it can prepare by carrying out grade churning, for example for 1 - 30 minutes until it mixes each component, it warms if needed (to about 50 degrees C) and it becomes homogeneity with agitators, such as a dissolver.

[0063] In the manufacture approach of the paint metal can of manufacture approach this invention of a paint metal can, the above-mentioned ultraviolet curing mold tin paint constituent is painted to the metal can which cast a metal plate, resin film laminated metal plates, or these metal plates, after irradiating ultraviolet rays and stiffening them, it prints on this hardening paint film, and, subsequently a clear coating is painted and stiffened.

[0064] As a coated object which paints this invention coating constituent For example, a tin plate, aluminum, chromium plated tinfree steel, iron, zinc, metal plate [, such as copper, a galvanized steel

sheet, and an alloy galvanized steel sheet of zinc and other metals, ]; -- chemical conversion metal plate; which performed chemical conversion to these metal plates -- to these metal plates and chemical conversion metal plates Polyolefin resin, such as polyester resin, such as polyethylene terephthalate, polyethylene, and polypropylene, The resin film laminated metal plate with which it comes to carry out the laminating of the resin films, such as polyamide resin, an epoxy resin, and a polyvinyl chloride; the can into which it comes to process these metal plates, a chemical conversion metal plate, or a resin film laminated metal plate can be mentioned.

[0065] The front face of the metal plate which is suitable for especially this invention coating constituent as a coating for base coats for can external surface, and molding processing is carried out with a can after paint especially as a painted surface of the above-mentioned coated object, and serves as can external surface, a chemical conversion metal plate, or a resin film laminated metal plate; it is suitable that a metal plate, a chemical conversion metal plate, or a resin film laminated metal plate is the can external surface which comes to carry out molding processing at a can.

[0066] this invention coating constituent can be painted by approaches, such as for example, roll coat paint, spray painting, brush coating, bar coat paint, roller coating, and silk screen printing.

[0067] Although what is necessary is just to choose the thickness of this invention coating constituent within limits from which a good coat appearance is acquired suitably, the range of about 2-8 micrometers is usually especially desirable [ thickness ] about 2-20 micrometers as desiccation thickness. What is necessary is just to choose exposure conditions suitably after applying a coat, according to the class and thickness of a coating constituent which were applied, although UV irradiation hardens after heating etc. removes a solvent, when a coat contains a solvent. As wavelength of the beam of light to irradiate, it is suitable, and within the limits of 200-450nm can usually use the source of an exposure which has wavelength with high sensibility, choosing it suitably.

[0068] As a source of an exposure of ultraviolet rays, a high-pressure mercury lamp, an extra-high pressure mercury lamp, a xenon lamp, a carbon arc, a metal halide lamp, sunlight, etc. can be mentioned, and, for the exposure conditions to a coat, dosage is usually 1 - 1000 mj/cm<sup>2</sup>. It is especially 50 - 500 mj/cm<sup>2</sup>. The becoming range is suitable.

[0069] In this invention approach, it prints on the hardening paint film which UV irradiation of this invention coating constituent was carried out [ paint film ], and stiffened it, and, subsequently a clear coating is painted and stiffened. Especially, the printing ink of itself known with which the ink used for the above-mentioned printing is used for printing of a package film can be used without a limit, and the method of application of printing ink can also perform it by the same approach as printing of a package film. As printing ink, it is desirable that it is heat-resistant ink of a heat bridge formation mold or an ultraviolet curing mold, for example, it can mention the printing ink of a polyester resin system, an acrylic resin system, and an alkyd resin system.

[0070] As a clear coating painted after applying ink, the clear coating of itself known according to the application can be used, for example, clear coatings, such as acrylic resin, polyester resin, an epoxy resin, vinyl chloride resin, and an acrylic-epoxy resin system, can be mentioned.

[0071] A clear coating may be painted and stiffened after stiffening ink. Moreover, a clear coating does not stiffen ink, may be painted in a wet-on sentiment on it, and may make a clear coating and coincidence harden ink. As the hardening approach, heat hardening, hardening by UV irradiation, etc. can be mentioned. When stiffening coincidence, it is desirable to also use a clear coating as a heat-curing mold coating, if ink is a heat-curing mold, and to also use a clear coating as an ultraviolet curing mold coating on the other hand, if ink is an ultraviolet curing mold.

[0072]

[Example] An example explains this invention more concretely. In addition, each of "sections" and "%" shall be hereafter based on weight criteria.

[0073] It warmed to 95 degrees C, teaching and agitating the toluene 500 section in the flask equipped with example of manufacture manufacture 1 agitator and condensator of a glycidyl group content copolymer. Subsequently, after dropping into this the glycidyl methacrylate 125 section, the styrene 375 section and 2, and the mixture that carried out the mixed dissolution of the 2'-azobisisobutyronitril 50

section beforehand over 4 hours and performing a polymerization, holding to this temperature, vacuum distillation removed toluene and the glycidyl group content copolymer (it is displayed as a "GMA copolymer" among the after-mentioned table 1) was obtained. The obtained copolymer had number average molecular weight 3,000 [ about ], the glycidyl group concentration of 1.8Eq/kg, and glass-transition-temperature (T<sub>g</sub>)85 degree C.

[0074] Into the example of manufacture manufacture 2 reaction container of ink, the phthalic anhydride 54 weight section, the adipic-acid 53 weight section, the trimethylol propane 81 weight section, the neopentyl glycol 38 weight section, and the linseed oil fatty-acid 60 weight section were blended, the heating dehydration condensation reaction was performed, and the alkyd resin of the acid number 10 was obtained. Organic red-pigments IRGAZIN DPP Rubine FTX [ of 20 weight sections ] (product made from tiba special tee KEMIKARUZU) and AF-5 solvent (the Nippon Oil Co., Ltd. make, aliphatic hydrocarbons) was enough kneaded with 3 rolls after 5 weight \*\*\*\*\* to this resin 100 weight section, AF-5 solvent was added, preparing a tuck with an inkometer, in order to consider as the tuck which was suitable subsequently to printing, and alkyd system oiliness red ink was obtained. The amount of as [ used ] AF-5 of the whole was about 10%.

[0075] The ethylene-glycol-monobutyl-ether 30 section was taught to the reactor equipped with example of manufacture manufacture 3 agitator, the condensator, the temperature controller, and nitrogen gas entrainment tubing of an aquosity clear coating, and it warmed to 120 degrees C. Into this, the mixed liquor of the azobisisobutyronitril 10 section which are the styrene 30 section, the methyl methacrylate 20 section, the 2-ethylhexyl methacrylate 18 section, the plaque cel FM3 (Daicel Chemical Industries, Ltd. make, lactone denaturation methacrylate, 100% of solid content) 18 section, the 2-hydroxyethyl methacrylate 10 section, the acrylic-acid 4 section, and a polymerization initiator was dropped over 3 hours, maintaining this temperature. Furthermore, after riping at this temperature for 1 hour, the mixed liquor of the azobisisobutyronitril 1 section and the ethylene-glycol-monobutyl-ether 10 section was dropped over 1 hour, and it was made to ripe at this temperature for 3 hours, and the acrylic resin solution of 71% of solid content was obtained.

[0076] The Cymel 325 (product [ made from Mitsui SAITEKKU ], methyl ether-ized melamine resin, 80% of solid content) 15 section, ethylene-glycol-monobutyl-ether 9 section, N, and N-dimethylamino ethanol 1.4 section was added to the acrylic resin solution 39 section obtained above, and stirring mixing was carried out. Subsequently, after adding the Nacure4167 (NEIKYUA 4167, made in [ King Industries ], phosphoric-acid system acid-catalyst, 25% of active principles) 3.2 section (active principle 0.8 section) and carrying out stirring mixing at homogeneity, deionized water was taught gradually, stirring and the aquosity clear coating of 40% of solid content was obtained.

[0077] manufacture example 1 SAIRA cure UVR-6110 (notes 1) (the after-mentioned table -- 1 inside) of an ultraviolet curing mold coating constituent the 50 sections displayed as "UVR-6110", and 3-ethyl-3-hydroxymethyloxetane (the after-mentioned table -- 1 inside) the 30 sections displayed as "OXA", and 3-ethyl-3-n-octyl oxymethyloxetane (the after-mentioned table -- 1 inside) the ten sections displayed as "OX-1", the CAT001 (notes 2) 10 section, and SAIRA cure UVI-6990 (notes 3) (the after-mentioned table -- 1 inside) The five sections displayed as "UVI-6990", the PHOTOINITIATOR 2074(notes 4) (it is displayed as "PI2074" among after-mentioned table 1) 1 section, and the high print 30T (notes 5)15 section were mixed and agitated, and the uniform ultraviolet curing mold coating constituent was obtained.

[0078] (notes 1) SAIRA cure UVR-6110 : a trade name, the U.S., made in Union Carbide, 3, 4-epoxycyclohexylmethyl -3, 4-epoxy cyclohexane carboxylate.

[0079] (notes 2) CAT001 : a trade name, a die cel and UCB company make, a fatty-acid modified epoxy resin.

[0080] (notes 3) SAIRA cure UVI-6990 : a trade name, the U.S., made in Union Carbide, PF6- Triaryl sulfonium salt system cationic initiator which it has.

[0081] (notes 4) PHOTOINITIATOR 2074 : a trade name, the "photograph initiator 2074", the Rhone-Poulenc S.A. make, a diaryl iodonium salt system cationic initiator.

[0082] (notes 5) High print 30T : a trade name, the Toyo Aluminium K.K. make, the leafing mold

aluminum paste that processed the aluminum front face with stearic acid, and a water surface diffusion area are 30000cm<sup>2</sup>/g.

[0083] In examples 2-9 and one to example of comparison 5 example 1, except carrying out as presentation combination is shown in the following table 1, it carried out like the example 1 and each ultraviolet curing mold coating constituent was obtained.

[0084]

[Table 1]

	表1 実施例						
	1	2	3	4	5	6	7
OX-1	10	30					
OX-2 (*1)			30	70			30
OX-3 (*2)					30		
OX-4 (*3)						30	
OX-5 (*4)							
OX-6 (*5)							
UVR-6110	50	50	50	30	50	50	50
OXA	30						
CAT001	10	20	20		20	20	20
GMA共重合体							
エポキシ化PB(*6)							
UVI6990	5	5	5	5	5	5	5
PI2074	1	1	1	1	1	1	1
ハイプリント30T	15	15	15	15	15	15	
ハイプリント50T(*7)							10

[0085]

[Table 2]

	表1 (続き)						
	実施例		比較例				
	8	9	1	2	3	4	5
OX-1				80			
OX-2 (*1)	30						
OX-3 (*2)		30					
OX-4 (*3)							
OX-5 (*4)					30		
OX-6 (*5)						30	70
UVR-6110	50	50	60		50	50	30
OXA			30	10			
CAT001			10		20	20	
GMA共重合体	20						
エポキシ化PB(*6)		20					
UVI6990	5	5	5	5	5	5	5
PI2074	1	1	1	1	1	1	1
ハイプリント30T	15	15	15	15	15	15	15
ハイプリント50T(*7)							

[0086] the inside of Table 1 -- it can set (\*\*) -- the semantics as following is expressed, respectively.

(\*1) OX-2:3-ethyl-3-(2-ethylhexyl oxymethyl) oxetane.

(\*2) OX-3:3-ethyl-3-dodecyl oxymethyloxetane.

(\*3) OX-4:3-ethyl-3-(3, 7-dodecadienyl oxymethyl) oxetane.

(\*4) OX-5:3-ethyl-3-n-butyloxy methyl oxetane.

(\*5) OX-6:3-ethyl-3-tetra-eicosanyl oxymethyl oxetane.

(\*6) Epoxidation polybutadiene : weight-per-epoxy-equivalent about 200 molecular weight 4000 [ about ].

(\*7) High print 50T : a trade name, the Toyo Aluminium K.K. make, the leafing mold aluminum paste that processed the aluminum front face with stearic acid, and a water surface diffusion area are 50000cm<sup>2</sup>/g.

[0087] Each coating constituent obtained in creation above-mentioned each example and the example of

a comparison of a test color card is painted so that hardening thickness may become a chromium-plated-tinfree-steel plate with a thickness of 0.2mm with about 5 micrometers, using the metal halide lamp, UV irradiation was performed and the metallic paint film was stiffened so that energy dosage might serve as 150 mJ/cm<sup>2</sup> from the distance of 10cm with the painted surface of a paint plate.

[0088] Subsequently, the alkyd system oiliness red ink obtained in said example 2 of manufacture on this hardening metallic paint film was printed so that desiccation thickness might be set to about 1 micrometer. The area rate of printing was used as about 50% of the metallic paint film. Subsequently, the aquosity clear coating obtained in said example 3 of manufacture was painted, it baked for 2 minutes at 200 degrees C, the clear hardening paint film of about 5 micrometers of hardening thickness was formed, and the test color card was obtained so that a printing ink side and the whole metallic paint film side might be covered.

[0089] Based on the following test method, it examined [ test color card / which was obtained ] about the unsettled thing and the thing which carried out retorting which is the processing immersed in 125-degree C ebullition underwater for 30 minutes in an autoclave in a test color card as it is. The test result is shown in the after-mentioned table 2.

[0090] Test-method paint-film appearance: The painted-surface appearance estimated on the following criteria.

O : the surface deterioration of x:paint film which is a good painted-surface appearance and which is inferior in the smooth nature of \*\*:paint film for a while is remarkable.

[0091] Adhesion: The cross cut which reaches a base with a knife was put into the test color card, and exfoliation extent of a paint film when sticking cellophane adhesive tape in the cross-cut section, and exfoliating a tape in an instant was judged by the following criteria.

O : -- exfoliation of x:paint film exfoliation of \*\*:paint film exfoliation of O:paint film exfoliation of a paint film is not accepted to be at all is slightly accepted to be is considerably accepted to be is remarkable.

[0092] Abrasion [-proof] nature: The following criteria estimated the painted-surface condition when grinding, going and coming back to die length of 6cm one time in all, having applied the 500g load for the paint film side comrade of a test color card.

O : -- although a blemish is slightly accepted in O:paint film front face on which a blemish is not accepted in a paint film, the blemish which reaches x:base in which a blemish is considerably accepted in \*\*:paint film front face which is practical use within the limits is accepted.

[0093] Pencil degree of hardness: It is JIS to each test color card. K5400 The pencil scratch test specified to 8.4.2 (1990) was performed, and evaluation by the tear method was performed.

[0094] Shock resistance: JIS K-5400 According to 8.3.2 (1990), impact processing was performed to the test color card from the opposite side of a paint film side using the E. I. du Pont de Nemours impact tester on the diameter of 3/8 inch of an impact core, 500g of falling weight loads, and conditions with a falling weight height of 50cm, the processing section was observed with the microscope, and the following criteria estimated.

O : -- O: as which peeling of a paint film is not regarded for a crack at all, either -- \*\*: as which peeling of a paint film is not regarded although a crack is seen slightly -- [0095] as which peeling of x:paint film as which peeling of a paint film is not regarded although a remarkable crack is seen is regarded [Table 3]

表2

		実施例						
		1	2	3	4	5	6	7
塗膜外観	未処理	◎	◎	◎	◎	◎	◎	◎
	UV処理	◎	◎	◎	◎	◎	◎	◎
密着性	未処理	◎	◎	◎	◎	◎	◎	◎
	UV処理	◎	◎	◎	◎	◎	◎	◎
耐擦り傷性	未処理	◎	◎	◎	◎	◎	◎	◎
	UV処理	◎	◎	◎	◎	◎	◎	◎
鉛筆硬度	未処理	3H	3H	3H	3H	3H	3H	3H
	UV処理	3H	3H	3H	3H	3H	2H	3H
耐衝撃性	未処理	◎	◎	◎	◎	◎	◎	◎
	UV処理	◎	◎	◎	◎	◎	◎	◎

[0096]

[Table 4]

表2 (続き)

		実施例		比較例				
		8	9	1	2	3	4	5
塗膜外観	未処理	◎	◎	◎	◎	◎	◎	◎
	UV処理	◎	◎	◎	◎	◎	◎	◎
密着性	未処理	◎	◎	△	○	◎	○	○
	UV処理	◎	◎	X	X	△	△	X
耐擦り傷性	未処理	◎	◎	◎	◎	◎	◎	◎
	UV処理	◎	◎	◎	◎	◎	◎	◎
鉛筆硬度	未処理	3H	3H	2H	B	2H	H	B
	UV処理	3H	3H	F	B	H	H	B
耐衝撃性	未処理	◎	◎	◎	◎	◎	◎	◎
	UV処理	◎	◎	◎	◎	◎	◎	◎

[0097]

[Effect of the Invention] The ultraviolet curing mold coating constituent of this invention can be hardened by UV irradiation, is excellent in the adhesion over a printing ink layer or a clear paint film with a thin film, and can form the photoluminescent paint film excellent in paint film engine performance, such as a paint film appearance needed as a tin paint, workability, a degree of hardness, and retort-proof nature, without needing the facility containing nitrogen etc.

[0098] Moreover, the paint metal can which has the luminosity coat which was excellent in adhesion with a printing layer and a clear coat, and was excellent also in brightness, a paint film appearance, and the paint film engine performance by the manufacture approach of the paint metal can using the ultraviolet curing mold coating constituent of this invention can be offered.

[Translation done.]

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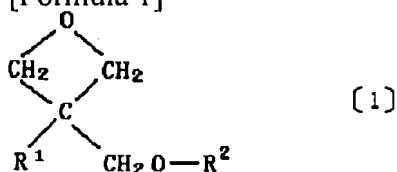
CLAIMS

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[Claim(s)]

[Claim 1] (A) The following type [1]

[Formula 1]



R1 expresses the shape of a hydrogen atom, a fluorine atom, and a straight chain of the carbon atomic numbers 1-6, a branched-chain or annular alkyl group, and a straight chain of the carbon atomic numbers 1-6, a branched-chain or annular fluoro alkyl group, an allyl group, an aryl group, an aralkyl radical, a furil radical, or a thienyl group among [type, and R2 expresses the shape of a straight chain, the branched-chain alkyl group, or alkenyl radical of the carbon atomic numbers 6-20. ] The ultraviolet curing mold tin paint constituent characterized by containing the cationic initiator 0.01 which comes out and generates a cation by (C) UV irradiation to the total quantity 100 weight section of the oxetane compound 1 shown - 80 weight sections, and cationic polymerization nature compounds 20 other than the (B) above-mentioned compound (A) - 99 weight sections - 20 weight sections, and the aluminium powder 1 with a mean particle diameter of 1-50 micrometers by which (D) stearic acid processing was carried out - 30 weight sections.

[Claim 2] The coating constituent according to claim 1 characterized by cationic polymerization nature compounds (B) being one sort or two sorts or more of combination of the compounds which have the compound and oxetane ring which have an alicyclic epoxy group.

[Claim 3] As some cationic polymerization nature compounds (B), it is the copolymer of a glycidyl group content polymerization nature partial saturation monomer and other polymerization nature partial saturation monomers. The copolymer whose glass transition temperature it has at least one glycidyl group in a molecule, and is 30 degrees C or more, The coating constituent according to claim 1 or 2 characterized by containing at least one sort in epoxidation polybutadiene and a fatty-acid modified epoxy resin below 40 weight sections to the total quantity 100 weight section of an oxetane compound (A) and a cationic polymerization nature compound (B).

[Claim 4] The manufacture approach of the paint metal can characterized by painting an ultraviolet curing mold tin paint constituent given in any 1 term of claims 1-3 to the metal can which cast a metal plate, resin film laminated metal plates, or these metal plates, printing on this hardening paint film after irradiating ultraviolet rays and stiffening them, and subsequently painting and stiffening a clear coating.

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[Translation done.]